

Ion Sensing with Poly(pyrrole) Based Membranes – Comparison Between Amperometric and Potentiometric Operation Mode

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Easy to obtain, ion-exchanging films of a conducting polymer (CP) are potentially highly useful for potentiometric and/or amperometric ion sensor construction. Both amperometric and potentiometric sensors utilise the ion exchange occurring between the polymer film and solution; analytically useful signal is either the current, related to ion exchange corresponding to polymer oxidation level change, or the alteration of the polymer membrane potential, respectively. Potentiometry with CP based membranes has been intensively studied over recent years[1,2], in contrary to amperometric detection of common ions, electrochemically inactive within the range of polymer electrochemical window. This topic was only briefly studied[3].

In the following work the possibility of amperometry with conducting polymer film using as an exemplary analyte, common ions (e.g. Cl^- or K^+) and poly(pyrrole) films is presented and compared to the potentiometry with polymer based ion-selective electrodes.

The changes of the current accompanying either anion-exchanging polymer film oxidation (e.g. poly(pyrrole) doped with chloride anions - PPyCl) or cation-exchanging polymer film reduction (e.g. poly(pyrrole) doped with hexacyanoferrate(II) ions - PPyFeCN) are dependent both on the potential applied and electrolyte concentration. It should be stressed that the crucial step of transduction of chemical information to electrical signal is the ion transfer through the polymer / solution interface. The chronoamperometric curves recorded for poly(pyrrole) films are usually of little analytical value since their shape changes for different electrolyte concentration, Fig 1. Thus the experiment conditions (mode and potential range) were optimised in order to obtain analytically useful dependencies: current vs. concentration. The corresponding results will be presented.

The exemplary relationship $\log(\text{current})$ vs. $\log(\text{concentration})$ of the optimised calibration graph obtained is presented in Fig 2 – recorded for poly(pyrrole) film doped with chloride anions. The similar dependence was obtained for poly(pyrrole) films obtained in the presence of hexacyanoferrate(II) ions. The effects of other electrolytes in the solution on the recorded calibration graphs were investigated. The results to be presented were critically evaluated and compared to these obtained for poly(pyrrole) based ion-selective electrodes.

The emphasis is on interferences effect on the transduction of the chemical information to the analytical signal. As the most important from point of view of the practical applications, the interferences of the redox couples present in solution and the effect of solution pH changes were considered. Their severe effect on open circuit potentials of conducting polymer films considerably limits their application as potentiometric sensors. The results obtained and presented herein point out that in many cases amperometry offers better possibilities of ion sensing in comparison to potentiometry in terms of sensitivity and robustness.

The future prospects and challenges of application of conducting polymer films to amperometric sensor construction are described.

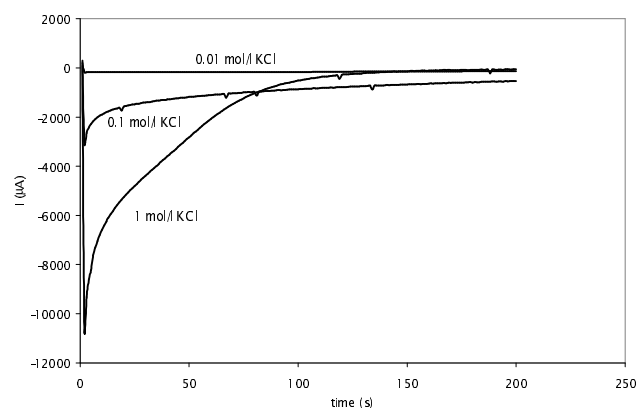


Fig 1. The chronoamperometric curves recorded for poly(pyrrole) film doped with hexacyanoferrate(II) ions, the film was oxidised at +0.4 V for 20 s, then the potential -0.1 V was applied and current changes were recorded.

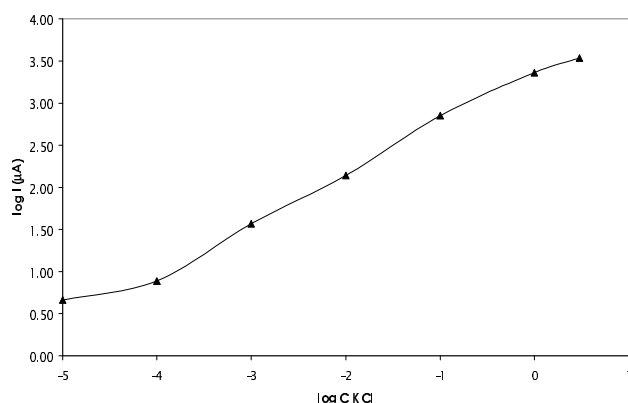


Fig 2. The amperometric calibration graph, $\log(\text{current})$ vs. $\log(\text{concentration})$ dependence, recorded for poly(pyrrole) film doped with chloride ions film in KCl solutions. The polymer electrode potential was changed from -0.5 V to $+0.5$ V, the current value was read 100 ms after $+0.5$ V potential step application.

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3. Y. Ikariyama, W. R. Heineman, *Anal. Chem.*, 58, **1986**, 1803.